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54 **Photo-curable composition.**

57 A photo-curable composition having a high photosensitivity which comprises a photopolymerizable monomer and, as a photopolymerization initiation system, an aromatic ketone and an amine, characterized in that at least a portion of said monomer and/or said amine is an amine having an acryloyl or methacryloyl group in the molecule.

**EP 0 262 242 A1**

**PHOTO-CURABLE COMPOSITION**

The present invention relates to a photo-curable composition. More particularly, it relates to a photo-curable composition improved in photosensitivity which comprises a photopolymerizable monomer and a photopolymerization initiation system comprising an aromatic ketone and an amine.

In general, photo-curable compositions comprise photopolymerizable monomers and photopolymerization initiators, frequently with polymeric materials. Among various photopolymerization initiators usable in such photo-curable compositions, there is known a photopolymerization initiation system comprising an aromatic ketone and an amine. This initiation system is frequently used because of such a meritorious property that its polymerization initiation is hardly inhibited by oxygen. However, said initiation system requires the use of an amine in a large amount for sufficient photopolymerization initiation, and as the result, the hardness of the cured resin composition is not adequate so that some roughness is produced at the surface and also the resolving power is lowered.

In order to overcome said drawbacks as seen in conventional photo-curable compositions comprising an aromatic ketone and an amine as the photopolymerization initiation system, an extensive study has been made. As the result, it has now been found that the use of such a specific amine as having an acryloyl or methacryloyl group in said initiation system can more hardly accept the unfavorable influence of oxygen than the use of other amines and rather results in acceleration of the polymerization by oxygen. In any event, the photosensitivity of a photo-curable composition is highly enhanced by the use of said specific amine in combination with an aromatic ketone so that the curing can be achieved within a shorter period of time. Advantageously, said specific amine has an acryloyl or methacryloyl group and is itself photopolymerizable. Thus, said specific amine itself participates in photopolymerization and does not remain in its monomeric form after light exposure so that the surface characteristics of the cured resin composition is not deteriorated.

According to this invention, there is provided a photo-curable composition having a high photosensitivity which comprises a photopolymerizable monomer and, as a photopolymerization initiation system, an aromatic ketone and an amine, optionally with a polymeric material, characterized in that at least a portion of said monomer and/or said amine is an amine having an acryloyl or methacryloyl group in the molecule.

As the photopolymerizable monomer in the photo-curable composition of the invention, there may be employed any one chosen from various polymerizable compounds having an ethylenic double bond, of which typical examples are methyl acrylate, ethyl acrylate, n-propyl acrylate, beta-hydroxyethyl acrylate, beta-hydroxypropyl acrylate, polyethylene glycol monoacrylate, polypropylene glycol mono acrylate, polyethylene glycol diacrylate, polypropylene glycol diacrylate, methoxypolyethylene glycol monoacrylate, ethoxypolyethylene glycol monoacrylate, glycerol diacrylate, pentaerythritol diacrylate, trimethylolpropane triacrylate, tetramethylolmethane tetraacrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, beta-hydroxyethyl methacrylate, beta-hydroxypropyl methacrylate, polyethylene glycol monomethacrylate, polypropylene glycol monomethacrylate, polyethylene glycol dimethacrylate, polypropylene glycol dimethacrylate, methoxypolyethylene glycol monomethacrylate, ethoxypolyethylene glycol monomethacrylate, glycerol dimethacrylate, pentaerythritol dimethacrylate, trimethylolpropane trimethacrylate, tetramethylolmethane tetramethacrylate, acrylamide, N-methylolacrylamide, n-butoxymethylacrylamide, isobutoxyacrylamide, n-t-butyl acrylamide, methylenebis(acrylamide), ethylenebis(acrylamide), propylenebis(acrylamide), methacrylamide, N-methylolmethacrylamide, n-butoxymethylmethacrylamide, isobutoxymethacrylamide, n-t-butylmethacrylamide, methylenebis(methacrylamide), ethylenebis(methacrylamide), propylenebis(methacrylamide), etc. One or more of these monomers are usable in the photo-curable composition of this invention.

The photopolymerization initiation system comprises an aromatic ketone and an amine in combination. Any compound having an aromatic ring and a ketonic group within the molecule is usable as the aromatic ketone, of which examples are benzophenone, acetophenone, fluorenone, thioxanthone, anthraquinone, etc. Further, these compounds may optionally be substituted with any substituent such as a cyano group, a nitro group, a methoxy group or a sulfonic group. One or more chosen from these aromatic ketones may be employed. As the amine, there may be used any conventional amine such as dimethanolamine, diethanolamine, triethylamine, etc. One or more of these amines are usable.

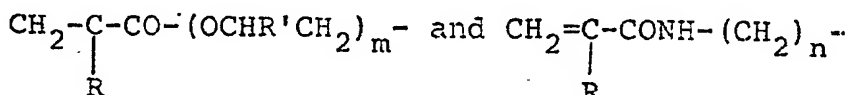
As stated above, it is characteristic in the photo-curable composition of the invention that at least a portion of the photopolymerizable monomer and/or the amine in the photopolymerization initiation system is an amine having an acryloyl or methacryloyl group. In other words, said polymerizable monomers and/or said conventional amines may be partly or totally replaced by one or more acryloyl or methacryloyl group-containing amines. When the acryloyl or methacryloyl group-containing amine is used as one of the

photopolymerizable monomers, it can simultaneously play a role as an essential component in the photopolymerization initiation system. Likewise, the acryloyl or methacryloyl group-containing amine used as an essential component in the photopolymerization initiation system can simultaneously play a role of the photopolymerizable monomer.

The acryloyl or methacryloyl group-containing amine may be representable by the formula:



wherein  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are each a hydrogen atom, a lower alkyl group (e.g. methyl, ethyl, n-propyl, isopropyl) or a group of either one of the following formulas:



(1)

(2)

wherein R and R' are each a hydrogen atom or a methyl group, m is an integer of 1 to 4 and n is an integer of 2 and 3, but at least one of  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  is a group of either one of the formulas (1) and (2). Specific examples are dimethylaminoethyl acrylate, diethylaminoethyl acrylate, dimethylaminopropyl acrylate, N,N-di-(acryloyloxyethyl)-ethylamine, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, dimethylaminopropyl methacrylate, N,N-di(methacryloyloxyethyl)methylamine, N,N-di-(methacryloyloxyethyl)ethylamine, N-(3-dimethylaminopropyl)acrylamide, N-(3-diethylaminopropyl)-acrylamide, etc. Among them, particularly preferred are those of the formula (I) wherein two of  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are either one of the formulas (1) and (2). These specific amines are per se known or may be prepared by per se known methods.

In addition to the above essential components, the photo-curable composition comprises frequently a polymeric material, of which examples are partially saponified poly-vinyl acetates, cellulose derivatives, polyethylene oxide, sodium polyacrylate, polyamides, etc.

The weight proportion of (a) the photopolymerizable monomer, (b) the photopolymerization initiation system comprising the aromatic ketone and the amine and (c) the polymeric material is usually about 100 : 0.001 - 10 and 0 - 300. The molar proportion of (b-1) the aromatic ketone and (b-2) the amine in the photopolymerization initiation system is about 1 : 1 - 30. The above weight proportion as well as the molar proportion are applicable to the case wherein said monomer and/or said amine are partly or totally replaced by said acryloyl or methacryloyl group-containing amine.

When the amine in the photopolymerization initiation system is totally replaced by the acryloyl or methacryloyl group-containing amine and any other amine is not used, the weight proportion of (a) the photopolymerizable monomer, (b) the photopolymerization initiation system and (c) the polymeric material is preferred to be about 0 - 500 (particularly 50 - 150) : 100 : 0 - 800 (particularly 20 - 400), and the molar proportion of (b-1) the aromatic ketone and (b-2) the amine in the photopolymerization initiation system is favored to be about 1 : 5 - 500 (particularly 1 : 15 - 100).

The photo-curable composition of the invention may further comprise any conventional additives such as polymerization inhibitors (e.g. 2,6-di-t-butyl-p-cresol, hydroquinone, p-methoxyphenol) and dyestuffs (e.g. Rose Bengal, Eosine, Methylene Blue, Malachite Green).

Preparation of the photo-curable composition can be carried out by admixing the above essential and optional components, if necessary, with water or any appropriate organic solvent.

The photo-curable composition thus prepared can be used itself as a photo-curable ink or a photo-curable paint or molded into any optional shape to use as a photo-curable printing plate.

Practical and presently preferred embodiments of the invention are illustratively shown in the following Examples and Comparative Examples, wherein part(s) are by weight unless otherwise indicated.

Example 1

Into a solution of N,N-dimethylaminoethyl methacrylate and trimethylolpropane trimethacrylate (1 : 1 by weight), benzophenone was dissolved to make a concentration of 0.1 mol/liter. Oxygen gas was introduced into the resultant photo-curable composition for 10 minutes. The resulting composition was irradiated with a high pressure mercury lamp of more than 334 nm through a filter over a period of 90 seconds. The cured product was washed with tetrahydrofuran to remove the uncured monomer, followed by drying. The weight of the dried product was 49.50 % of the initial weight of the photo-curable composition. Likewise, the weights of the dried products when irradiated over periods of 150 and 240 seconds were respectively 66.23 and 80.25 % based on the initial weight of the photo-curable composition.

Comparative Example 1

In the same manner as in Example 1 but using triethylamine instead of N,N-dimethylaminoethyl methacrylate, curing was effected. The weights of the dried products when irradiated over periods of 90, 150 and 240 seconds were respectively 21.10, 32.62 and 34.90 % based on the initial weight of the photo-curable composition.

Example 2

In the same manner as in Example 1 but without introduction of oxygen, curing was effected. The weights of the dried products when irradiated over periods of 90, 150 and 240 seconds were respectively 40.70, 49.50 and 62.30 % based on the initial weight of the photo-curable composition.

Comparative Example 2

In the same manner as in Example 2 but using triethylamine instead of N,N-dimethylaminoethyl methacrylate, curing was effected. The weights of the dried products when irradiated over periods of 90, 150 and 240 seconds were respectively 15.90, 23.37 and 29.25 % based on the initial weight of the photo-curable composition.

Example 3

A photo-curable composition comprising the following materials was dried to make a photosensitive printing plate of 0.4 mm thick:

	<u>Part (s)</u>
45 % Aqueous solution of polyvinyl alcohol (saponification degree, 82 %; polymerization degree, 500)	50
N,N-Diethylaminoethyl methacrylate	10
Trimethylolpropane trimethacrylate	10
Benzophenone	0.4
Methoquinone	0.1

On the photosensitive printing plate, a Kodak step tablet No. 2 (21 steps) and then a polyethylene terephthalate film were placed in order, and the resulting piled product was placed under reduced pressure to make sure their close contacts, followed by irradiation with a high pressure mercury lamp (ORC Polymer Printer 3000) of 500 mj/cm<sup>2</sup>. The resulting cured plate was developed with water to remove uncured monomer. The resultant cured plate showed curing up to the 16th step.

### Comparative Example 3

In the same manner as in Example 3 but using triethanolamine instead of N,N-diethylaminoethyl methacrylate, the operation was effected. The resultant cured plate showed curing up to the 10th step.

In the same manner as above but with pre-irradiation (pre-exposure) of a light of 8 mj/cm<sup>2</sup> for consumption of the oxygen dissolved in the photo-curable composition, the operation was effected. The resultant cured plate showed curing up to the 14th step.

In both of the above cases, roughness was observed at the cured portion after water development.

### Example 4

In the same manner as in Example 3 but using N,N-di(methacryloyloxyethyl)methylamine instead of N,N-diethylaminoethyl methacrylate, the operation was effected. The resultant cured plate showed curing up to the 18th step.

### Comparative Example 4

In the same manner as in Example 4 but using triethanolamine instead of N,N-di(methacryloyloxyethyl)ethylamine, the operation was effected. The resultant cured plate showed curing up to the 10th step.

In the same manner as above but with preirradiation of a light of 8 mj/cm<sup>2</sup> for consumption of the oxygen dissolved in the photo-curable composition, the operation was effected. The resultant cured plate showed curing up to the 14th step.

In both of the above cases, roughness was observed at the cured portion after water development.

### Reference Example 1

Preparation of N,N-di(methacryloyloxyethyl)methylamine:-

To a 15 % tetrahydrofuran solution of diethanolmethylamine (1 mol), triethylamine (2 mol) as a catalyst was added, and a 10 % tetrahydrofuran solution of methacryloyl chloride (2 mol) in 10 % tetrahydrofuran solution was dropwise added thereto while stirring. Since the reaction proceeded with heat generation, occasional cooling with ice was effected. After completion of the dropwise addition, the reaction mixture was further stirred for about 30 minutes, and the precipitated salt was eliminated by filtration. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography using benzene as a developing solvent to give N,N-di(methacryloyloxyethyl)methylamine. The infrared absorption spectrum of this product is as shown in Fig. 1 of the accompanying drawing. The characteristic values in the NMR spectrum are as shown below: 4.20 (doublet) = CH<sub>2</sub> (4H); 5.68 (triplet) -CH<sub>2</sub>O (4H); 7.22 (triplet) -NCH<sub>2</sub>- (4H); 7.62 (singlet N-CH<sub>3</sub>) (3H); 8.40 (singlet) C(CH<sub>3</sub>) = (6H).

### Reference Example 2

Preparation of N,N-di(methacryloyloxyethyl)ethylamine:-

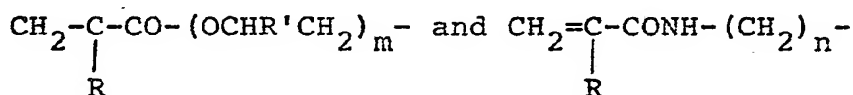
In the same manner as in Reference Example 1 but using diethanoethylamine instead of diethanolmethylamine, there is produced N,N-di(methacryloyloxyethyl)ethylamine.

## Claims

1. A photo-curable composition having a high photosensitivity which comprises a photopolymerizable monomer and, as a photopolymerization initiation system, an aromatic ketone and an amine, characterized in that at least a portion of said monomer and/or said amine is an amine having an acryloyl or methacryloyl group in the molecule.
2. The composition according to claim 1, which comprises further a polymeric material.
3. The composition according to claim 1, wherein the amine in the photopolymerization initiation system is totally replaced by the acryloyl or methacryloyl group-containing amine.
4. The composition according to claim 1, wherein the weight proportion of the monomer and the photopolymerization initiation system is 100 : 0.001 - 10.
5. The composition according to claim 4, wherein the molar proportion of the aromatic ketone and the amine in the photopolymerization initiation system is 1:1 - 30.
6. The composition according to claim 1, wherein the weight proportion of the monomer and the photopolymerization initiation system is 0 - 500 : 100.
7. The composition according to claim 6, wherein the molar proportion of the aromatic ketone and the amine in the photopolymerization initiation system is 1 : 5 - 500.
8. An amine of the formula:



wherein R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are each a hydrogen atom, a lower alkyl group or a group of either one of the following formulas:



(1)

(2)

wherein R and R' are each a hydrogen atom or a methyl group, m is an integer of 1 to 4 and n is an integer of 2 and 3, but two of R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are each a group of either one of the formulas (1) and (2).

9. The amine according to claim 8, which is N,N-di(methacryloyloxy(lower)alkyl)-lower alkylamine.
10. The amine according to claim 9, which is N,N-di(methacryloyloxyethyl)methylamine.
11. The amine according to claim 9, which is N,N-di(methacryloyloxyethyl)ethylamine.



EP 86 11 3457

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	CHEMICAL ABSTRACTS, vol. 91, no. 18, October 1979, page 67, abstract no. 142163h, Columbus, Ohio, US; & JP-A-79 62 235 (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD) 19-05-1979 * Whole abstract *  -----	1-11	C 08 F 2/50 G 03 C 1/68
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 F G 03 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 25-06-1987	Examiner CAUWENBERG C.L.M.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons  & : member of the same patent family, corresponding document	